Influence of acid treatments of carbon nanotube precursors on Ni/CNT in the synthesis of carbon nanotubes

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Abstract

The Ni/CNT catalyst was fabricated by directly dipping carbon nanotube precursors refluxed in 4 M of nitric acid into Ni electroless plating bath, and used to synthesize new carbon nanotubes. The experimental results indicate that the duration of acid-treatment of carbon nanotubes precursors exerts a great influence on the catalysis of Ni/CNT in the synthesis of carbon nanotubes and hence the structures of the new carbon nanotubes. When the carbon nanotubes precursors were refluxed for 0.5 h in 4 M of nitric acid, bamboo-shaped carbon nanotubes (BSCNT) or Y junction carbon nanotubes in the carbon products were obtained. As the duration of acid-treatment of carbon nanotubes precursors increased to 6 h, the as-prepared Ni/CNT displayed higher activity, and the carbon nanotube products were high pure without any Y junction structure or any separation layers in hollow.
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Keywords: Carbon nanotubes; Ni/CNT; Bamboo-shaped structure; Y junction

1. Introduction

In 1976, the group of Endo first synthesized carbon "filaments" through the pyrolysis of mixtures of benzene and hydrogen by metallic catalyst particles at 1100 °C [1]. In 1991, Iijima fabricated carbon nanotubes (CNTs) by arc-discharge [2]. After that, extensive interests were focused on the fabrication of carbon nanotubes. Due to its low cost and large-scale production capacity, the catalytic decomposition of hydrocarbon has become one of the most important synthesis methods for carbon micro- and nano-structures [3–5]. It has been established that the use of certain form of Fe, Co or Ni metal particles highly dispersed on all kinds of substrates as catalysts is essential for the growth of preferred carbon structures [6–10]. However, the removal of some kinds of substrates such as SiO_2, Al_2O_3 may be quite

difficult before their application. Cylindrically layered and hollow tubular nano-structures with their high thermal and chemical stability make it possible for carbon nanotubes to function as supports for preparing nano-sized metal and metal oxide particle catalysts [11–14]. Thus there is no need for the removal of substrate when the Ni/CNT is used for the synthesis of new carbon nanotubes. Rh/P [12], Pt–WO_3 [13] and Pt [14] catalysts supported on carbon nanotubes have been studied and shown to have exceptional properties. The deposition of nickel on carbon nanotubes has also been reported [15–17]. Baker and co-workers [18–19] have reported that Ni decorating carbon nanofibers, exhibits a high catalytic activity when compared to classical supported catalysts, for light hydrocarbon hydrogenation reactions in the gas-phase, at atmospheric pressure. It was suggested by the authors that when nickel is supported on graphite nanofibers, the metal crystallites adopt a different morphology, i.e. hexagonal thin morphology, compared to those observed when the nickel is dispersed on classical support carriers such as alumina or silica. Such a peculiar metal morphology observed on

the carbon nanofiber carrier was considered to be due to a strong metal-support interaction between nickel crystallites and exposed graphite planes. In our experiments, carbon nanotube-supported Ni catalyst also shows high catalytic activity in the synthesis of carbon nanotubes at $700\,^{\circ}C$.

In this paper, carbon nanotubes used as supports were refluxed in the dilute nitric acid and directly immersed in the Ni electroless plating bath for the Ni deposition. The results suggested that the duration of acid-treatment of carbon nanotube supports affects the preparation and catalytic properties of Ni/CNTs greatly. And we postulate a possible mechanism for this influence.

2. Experimental

The carbon nanotube precursors served as supports were fabricated by pyrolysis of xylene at about $1100\,^{\circ}C$ in a quartz tube furnace. In order to study the influence of the duration of acid treatment on the catalytic properties of Ni/CNT catalysts in the synthesis of carbon nanotubes, Ni supported on carbon nanotubes acid-treated for 6 and 0.5 h were used for the catalytic decomposition of C_2H_2. The carbon nanotube supports were acid-treated as follows: the carbon nanotubes were first refluxed in 4 M of nitric acid solution and were then filtered with a ceramic filter, washed with distilled water up to neutralization and dried.

Nickel catalyst was introduced onto the surface of carbon nanotubes by using electroless-plating method. The carbon tubes supports (0.50 g) acid-treated were dispersed into 10 ml ethanol (99.7%) and the suspension stirred in the Ni bath of composition $NiSO_4 \cdot 6H_2O$, 10 g/l; $C_4H_4O_6KNa \cdot 4H_2O$, 45 g/l; NaOH, 5 g/l; HCHO (38 wt.%), 16 ml/l. After 15 min, the mixture was filtered through a ceramic filter, washed several times with distilled water and dried up in air at $80\,^{\circ}C$. As a consequence, the nano-sized particles supported on CNTs were obtained.

The two catalyst precursors (0.05 g), Ni supported on carbon nanotubes acid-treated for 0.5 and 6 h, were spread in two ceramic boats, respectively and then placed in the reaction re-

gion of a horizontal CVD quartz tube furnace. The reaction region was heated to $580\,^{\circ}C$ under nitrogen and nitrogen substituted by hydrogen at a flow rate of 200 ml/min for 30 min, and subsequently the catalyst was reduced. The reaction region was heated to $700\,^{\circ}C$ in hydrogen and ethyne introduced with a flow rate of 100 ml/min. The catalytic decomposition reaction proceeded for 30 min. Then the products were cooled to room temperature under nitrogen and the boat with the reaction products was taken out. The black powder produced was dispersed onto a supported membrane for transmission electron microscopy.

For the removal of the amorphous carbon and metallic catalyst in the product, the raw soot produced was first suspended in 0.2 l of 4 M diluted nitric acid and refluxed at $117\,^{\circ}C$ for 2 h. Then the solution was filtered and rinsed with pure water up to neutral and dried. Finally pure carbon nanotubes were obtained.

Transmission electron microscopy (TEM) was used to observe the microstructures and morphologies of Ni/CNTs catalyst and new carbon nanotubes and EDX used to determine the elemental compositions of the Ni particles on the carbon nanotubes.

3. Results and discussions

Fig. 1 shows the micrographs of the nickel catalyst supported on carbon tubes acid-treated differently. From Fig. 1, when carbon nanotubes precursors were refluxed for 0.5 h, the Ni particles deposited are spherical with the average diameters about 65 nm and the metal-support contact area is smaller than the diameters of Ni particles. As the acid pretreatment duration of carbon nanotube precursors increased to 6 h, the density of the Ni-particles-deposited and the metal-support contact area increased while the average particle size decreased to about 58 nm, indicating higher dispersion of the Ni particles.

The specific surface area (SSA) of both the catalysts and the supports were calculated from the adsorption isotherm of nitrogen at liquid nitrogen temperature using the
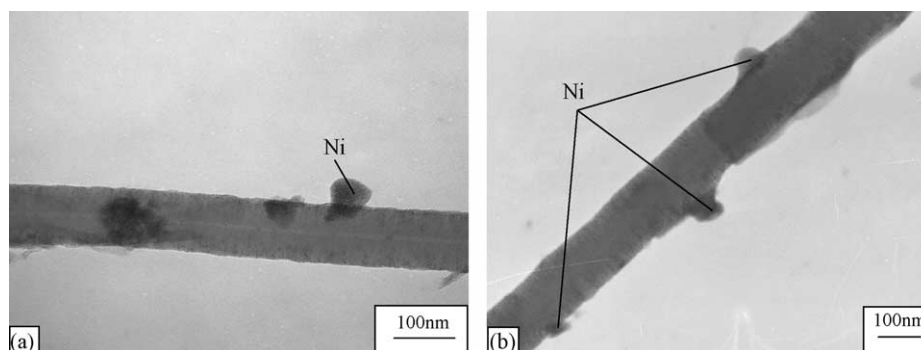

Fig. 1. Micrographs of Ni-deposited carbon tubes (a) carbon nanotubes precursors refluxed in 4 M of nitric acid for 0.5 h; (b) carbon nanotubes precursors refluxed in 4 M of nitric acid for 6 h.
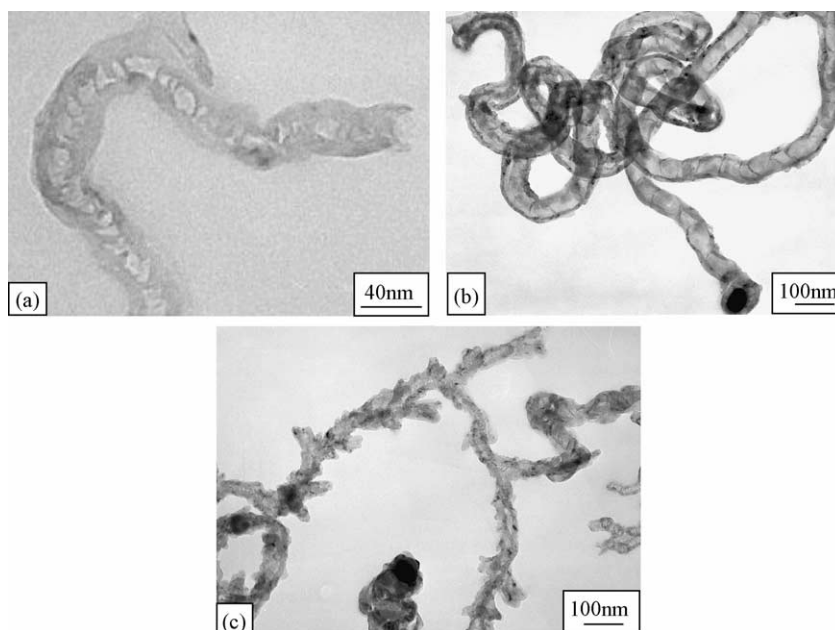
Fig. 2. Morphologies of carbon nanotubes synthesized with nickel catalyst supported on carbon nanotubes acid-treated for 0.5 h in dilute nitric acid.

Brunauer–Emmett–Teller (BET) sorption apparatus. The results show that the SSA of carbon nanotubes supports acid-treated for 0.5 and 6 h are 123 and 138 m^2/g, respectively, and the SSA of the corresponding Ni/CNT catalysts increased to 144 and 176 m^2/g.

The above two Ni/CNT catalysts produced were employed to synthesize new carbon nanotubes. And TEM analysis was performed on the new carbon nanotubes to determine the wall structure. The TEM image in Fig. 2 shows the diversified micrographs of carbon nanotubes synthesized with nickel catalyst supported on carbon nanotubes acid-treated for 0.5 h. It can be seen that new carbon nanotubes are curvous multi-walled CNTs with various diameters ranging from 40 to 80 nm. Fig. 2a and b indicate one kind of structure of the carbon nanotube products with many separation layers in hollow, looking like the bamboo. The inside of CNT is hollowed without any catalyst particles and the root is opened. From Fig. 2a, the surface of carbon nanotubes is not so smooth and seemed to be covered by amorphous carbon. Fig. 2b shows that the separation layers are conical shaped graphite layers directed to the open root of the carbon nanotubes and appear at larger distance. However, the diameter is not uniform: the diameter of the root is larger than that of the tip. Fig. 2c shows the TEM image of Y junction structure of carbon nanotubes products. It can be seen that carbon nanotube stem has many carbon nanotubes branches. Some branches are capped while others continue to grow.

The carbon nanotubes synthesized with nickel catalyst supported on carbon nanotubes acid-treated for 6 h have better morphologies (as shown in Fig. 3). They are high purity multi-walled nanotubes, either straight or curved, without any separation layers in hollow or Y branches, with outer and inner diameters ranging from 30 to 70 and 10 to 20 nm, respec-

tively and length up to several tens of micrometers. Compared with the size distribution of the originally deposited Ni particles, the outer diameters of the carbon nanotubes produced show a wider distribution at the extremes, which is consistent with the results of reference [20]. From Fig. 3a, one can see that the carbon nanotube products seemed to grow from carbon nanotube supports. And Fig. 3c shows Ni catalyst particles are encapsulated in the middle of the carbon nanotubes, indicating that the growth mechanism of the carbon nanotubes obey the open-ended models [21].

Carbon yields of the two products are calculated as follows: carbon yield = $100 \times$ (mass of product − mass of catalyst)/mass of catalyst. The results indicate that the carbon yield of the product (1100%) synthesized with Ni supported on carbon nanotubes acid-treated for 6 h is about 29% larger than that (850%) synthesized with Ni supported on carbon nanotubes for 0.5 h.

According to the above results, the Ni catalyst supported on carbon nanotubes acid-treated for 6 h exhibits higher SSA, metal dispersion and catalytic activity than that supported on carbon nanotubes acid-treated for 0.5 h. Since the two catalysts have been prepared using the same procedure, the higher activity of Ni supported on carbon nanotubes acid-treated for 6 h together with higher SSA and dispersion of the active phase is ascribed to the increasing duration of the acid-treatment of the carbon nanotube supports.

As the duration of the acid-treatment increased from 0.5 to 6 h, the interaction of the nanotubes with HNO_3 opened the caps and broke the tubes at imperfections, giving rise to shorter nanotubes. Thus a fraction of end planes, inner cavities and imperfect outer surfaces contribute to the increment of SSA. So the SSA of carbon nanotubes acid-treated for 6 h is about 12% larger than that of the carbon nanotubes acid-
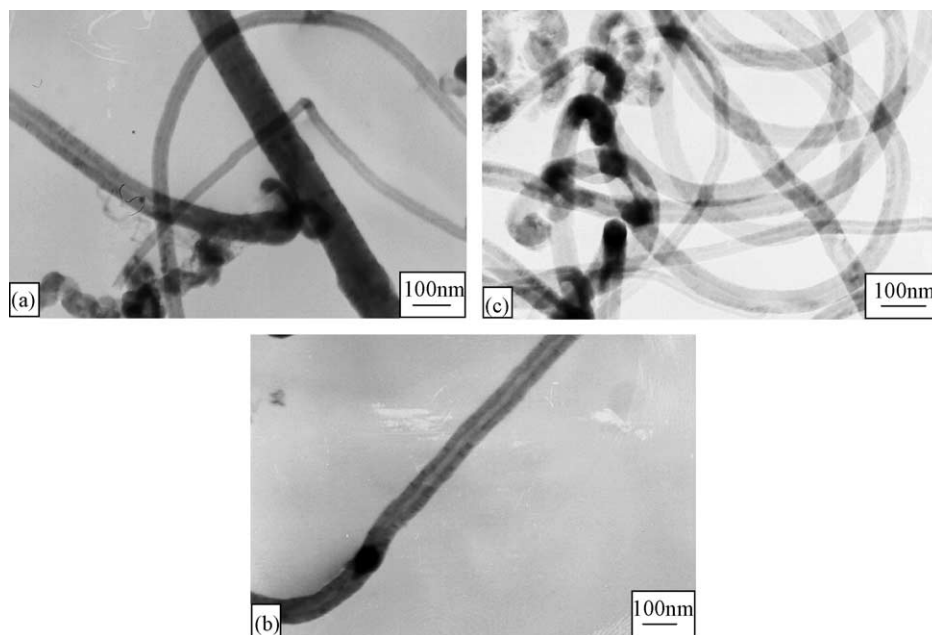
Fig. 3. Morphologies of carbon nanotubes synthesized with nickel catalyst supported on carbon nanotubes acid-treated for 6 h in dilute nitric acid.

treated for 0.5 h, and the trend is similar for the SSA of the catalyst. The larger SSA of carbon nanotubes will benefit Ni catalyst dispersion during the preparation of the nanotube-supported catalyst. In turn, the higher dispersion of Ni catalyst on carbon nanotubes will result in the increment of the SSA of the nanotube-supported catalyst.

In addition, the acid-treatment of carbon nanotubes also introduced the functional groups [22–23], such as hydroxyl (−OH), carboxyl (−COOH) and carbonyl (>C=O), especially for the sites with imperfections. Since the Ni deposition entails contacting the carbon nanotubes with the solution of the catalyst precursor, and carbon nanotubes are essentially nonhydrophilic in nature, they have a very low affinity for solvents of polar character such as water. The introduction of the acidic surface groups decreased the hydrophobicity of the carbon nanotubes and made the surface more accessible to the aqueous solution of the metal precursors or deposits [24]. Thus during the reactions, Ni^{2+} ions were reduced, conglomerated and formed Ni nano-particles on the carbon nanotubes. As the duration of the acid-treatment of carbon nanotubes supports increased from 0.5 to 6 h, more functional groups would be introduced onto the surface of carbon nanotubes, and the hydrophobicity of carbon nanotubes precursors would decrease. Therefore, more metal precursors are attached to the nanotubes and more metal particles are dispersed more homogeneously on the outer surface, leading to small diameters on the whole [24]. EDX analysis confirms this: the loadings of Ni increased from 3.71 to 5.62 at.% with the increasing duration of acid-treatment of carbon nanotube precursors from 0.5 to 6 h. The smaller mean particle size and the larger metal-support contact area also indirectly proved this when the carbon nanotubes were acid-treated for 6 h.

Bamboo-shaped carbon tubes have been reported before [25–29], but the growth mechanism of this kind of tubes is not clearly understood. In our work, the base growth mechanism is suitable for the bamboo-shaped carbon nanotubes, according to hollow tip and open root (as shown in Fig. 2) [25–28]. At first, carbon atoms resulted from the decomposed hydrocarbon were absorbed on the bottom surface of the Ni particles, then dissolved in the particles and moved by diffusion and condensed gradually on the top surface, forming graphite sheets as a cap on the catalytic particles. In the growth reaction of CNTs, the diffusion of carbon atoms in the catalyst particles, including the surface diffusion and bulk diffusion, is believed to be the rate-determining step [25]. The vertical graphite sheets are grown by surface diffusion of carbon atoms and the separation layers of compartments are grown by bulk diffusion of carbon atoms [15–26,28].

The growth rate of CNTs can be described by an Arrhenius equation [25] that the activation energy is the diffusion energy of carbons in the metal. For nano-scaled Ni particles on the surface of carbon nanotubes, the activation energy on the surface is higher than that in the bulk of the Ni particles, which results in the higher diffusion rate of carbon atoms on the surface of the metal particles than in the bulk. As the carbon atoms are continuously added to the edge of cap, the cap of graphite sheets lifts off the catalytic particle. Then a closed tip with the inside hollow is formed. As the carbon nanotubes continue to grow, the carbon nanotubes with separation layers are formed. The motive force of lift-off of the cap at the catalytic particle may be the stress accumulated under the graphite cap [28].

From Fig. 2b, the separation layers of the carbon nanotubes appear at larger distance than that of the carbon

nanotubes in Fig. 2a. It is advisable that the carbon nanotubes in Fig. 2b were synthesized with the Ni particles deposited on the sites (such as imperfections) with more functional groups. Due to more functional groups, the stability of the Ni catalyst increased [30] and the outer crystal planes structure of nickel particles might be changed to benefit the surface diffusion of carbons [18–19,30], resulting in the increasing of surface diffusion rates of carbons. Therefore, the surface diffusion of carbon becomes dominant to the bulk diffusion of carbons. Since the separation layers are grown by bulk diffusion, the separation layers appear at larger distance.

The TEM image in Fig. 2c shows another kind of structure of carbon nanotubes products. The important feature of this kind of carbon nanotubes is Y junction. With regard to the Y junctions, the growth mechanism has not been clearly understood. The carbon nanotubes with Y junction structures were first found in the carbon deposit produced under specific arc-discharge conditions by Zhou and Seraphin [21]. They suggested that the joining of several carbon nanotubes formed L, Y, and T patterns. In contrast, Gan et al. [31] confirmed that Y junction CNTs are produced by a sequential growth process rather than a joining process, where the topological defects are indispensable in forming the bending angles. In other words, Y junction CNTs were prepared because pentagonal or heptagonal defects were introduced into the planarity of hexagonal networks in the growth process. It is suggested that the Ni catalyst particles should play critical roles in the Y junction formation.

From Fig. 2, the curvature of carbon nanotubes products is very serious. It is known to us that the catalytic effect of Ni particle is determined by its outer crystal planes and its morphologies [27]. If the catalyst is isotropic, then a straight carbon nanotubes may be formed. But the catalyst is often anisotropic, the growth rate of the wall of the tube around the catalyst particle may not be the same, thus the curved carbon nanotubes can be formed.

The carbon nanotubes synthesized with Ni supported on carbon nanotubes acid-treated for 6 h (as shown in Fig. 3) are better in quality than that synthesized with Ni supported on carbon nanotubes acid-treated for 0.5 h, indicating that the duration of acid-treatment of carbon nanotubes precursors exerts a great influence on the catalytic properties of Ni particles in the synthesis of carbon nanotubes. The mechanism of the influence of acid treatment might be mainly dependent on the smaller diameters of Ni catalyst. When the size of catalytic particle decreased with the increasing duration of carbon nanotube precursors from 0.5 to 6 h, the ratio of surface area to volume would increase rapidly and the surface energy increases greatly [24–25]. Therefore, it is expected that the surface diffusion becomes dominant in the growth of carbon nanotubes. Consequently, the separation layers in the carbon nanotubes disappear. Of course, as more functional groups are introduced to the surface of carbon nanotubes, the interaction between Ni particles and carbon nanotubes is enhanced and the outer planes of Ni particles might favor the surface diffusion of carbons more greatly, which may be an-

other important reason of the increasing of the activity of the Ni particles [18–19,30].

4. Conclusions

Acid treatment of the carbon nanotube precursors plays key roles for the Ni deposition and exerts a great influence on the properties of Ni catalyst in the synthesis of carbon nanotubes. When the carbon nanotubes substrates were refluxed in the nitric acid for 6 h, the Ni catalyst particles displayed high activity and the carbon nanotubes products have high quality and high purity. Therefore, the carbon nanotubes as catalyst support has a bright future in the field of catalyst.

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